

A Metal–Organic Nanotube Exhibiting Reversible Adsorption of (H₂O)₁₂ Cluster

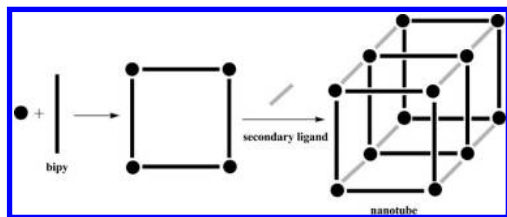
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Much effort has been focused on the investigation of water structures due to its fundamental importance in chemical and biological processes.¹ In particular, many small water clusters such as hexamers,² octamers,³ and decamers⁴ have been found as crystal hosts and structurally characterized, which provide information of understanding the behavior of bulk water. Recently, low-dimensional polymeric water/ice has also been structurally characterized and reported.⁵ In general, the small water cluster as well as polymeric water/ice coexist with other organic ligands or act as host in metal–organic frameworks. Thus, small water clusters may be trapped in porous materials such as metal–organic nanotubes (MONTs) or open frameworks due to their special porous property. In this communication, we report the synthesis and characterization of a novel metal–organic nanotube possessing reversible and fast adsorption of the (H₂O)₁₂ cluster.

Since the discovery of carbon nanotubes in 1991,⁶ many nanotubular structures containing elements other than carbon and different metal ions have been synthesized.⁷ Recently, considerable progress has been made in the design and synthesis of nanotubular metal–organic frameworks based on coordinative bonds because these porous materials have potential applications in gas storage and magnetism. Although many metal–organic frameworks (MOFs) with open channels have been synthesized in the past decades,⁸ only a few nanotubular MOFs have been reported in the literature. For instance, a nanotubular silver complex constructed from a flexible tripodal ligand and a nanotubular cadmium complex based on mixed organic ligands have been synthesized by Hong and co-workers.⁹ Zur Loye and co-workers reported a zinc tubular MOF based on a 3-amino-1,2,4-triazole ligand.¹⁰ Nanotubular 3d-4f heterometallic MOFs as well as a lanthanide tubular structure have also been designed and synthesized.¹¹ However, the nanotubular unit in the MOF mentioned above just acts as a subunit, which was further connected by other ligands to form a highly dimensional framework; the independent 1D metal–organic nanotubes (MONTs) are quite rare.¹²



To assemble 1D metal–organic nanotube, the linking mode of the organic ligand should meet with the coordination geometry of the metal ion. An effective strategy is that the metal ion is first connected by organic ligands to generate a square as the subunit, and then, the second organic ligands link the square subunits from the four vertexes to generate a 1D nanotubular framework. By using

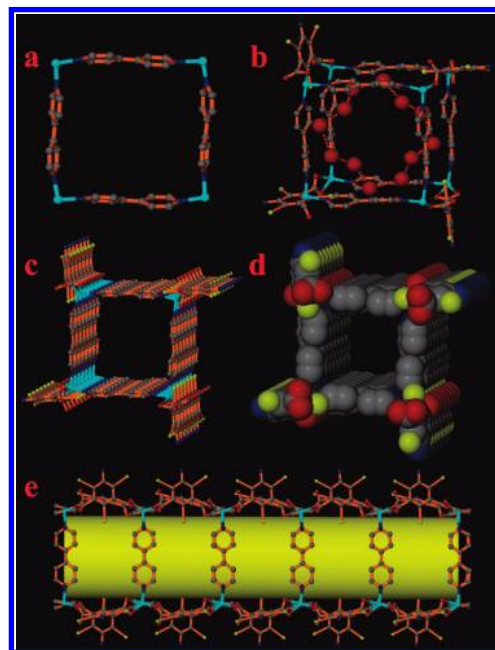


Figure 1. (a) Zn₄(bpy)₄ square; (b) Zn₈(bpy)₈(ATIBDC)₄ box trapped the (H₂O)₁₂ cluster; (c and d) 1D nanotube of **MONT-1** along *c* axis; (e) nanotubular structure of **MONT-1** showing the tube interior (yellow column).

this synthetic strategy, a novel 1D metal–organic nanotube, Zn(ATIBDC)(bpy)·3H₂O (**MONT-1**), constructed from 4,4'-bipy (bpy) and 5-amino-2,4,6-triiodoisophthalic acid (H₂ATIBDC), has been synthesized.

Slow diffusion of diethyl ether into a mixture of Zn(NO₃)₂·6H₂O, H₂ATIBDC and 4,4'-bipy in dmf/EtOH/H₂O (v/v = 5:2:1) resulted in the formation of a large amount of yellow prismatic crystals of **MONT-1**, which was structurally characterized by single-crystal X-ray diffraction. The formula of [Zn(ATIBDC)(bpy)]·3H₂O was further confirmed by elemental analysis and TGA.

Single-crystal X-ray diffraction reveals that **MONT-1** crystallizes in tetragonal space group *P4/n*. The asymmetric unit consists of one zinc ion, one ATIBDC, one bpy, and three uncoordinated water molecules. The central zinc ion is coordinated by two nitrogen atoms from two bpy ligands and two oxygen atoms from different ATIBDC ligands in a tetrahedral geometry. One of remaining carboxyl oxygen atoms has a weak coordination to the zinc ion with the Zn–O distance being 2.250 Å. The bpy ligand adopts a bidentate bridging mode to connect two zinc ions. Thus, four zinc ions are first linked by four bpy ligands to generate a [Zn₄(bpy)₄] square with the Zn–Zn distance being 11.168 Å (Figure 1a), which is similar to those found in other molecular squares.¹³

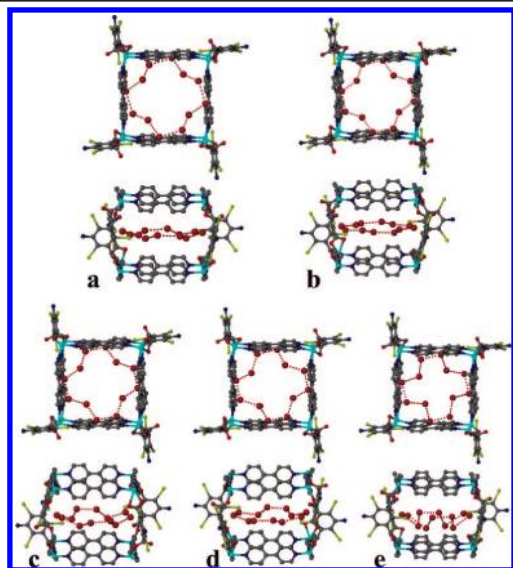


Figure 2. $(\text{H}_2\text{O})_{12}$ cluster trapped by $\text{Zn}_8(\text{bpy})_8(\text{ATIBDC})_4$ box. (a) Original and reabsorbed after heated to (b) 180, (c) 200, (d) 240, and (e) 280 °C.

Both carboxylate groups of ATIBDC are deprotonated during the reaction, and the whole ligand acts as a bridging linker to connect two zinc ions. Thus, the $[\text{Zn}_4(\text{bpy})_4]$ squares are infinitely connected by ATIBDC ligands along the c axis to give rise to a 1D metal–organic nanotube containing $\text{Zn}_8(\text{bpy})_8(\text{ATIBDC})_4$ boxes, in which $(\text{H}_2\text{O})_{12}$ clusters were trapped. The $\text{Zn}_8(\text{bpy})_8(\text{ATIBDC})_4$ box has the dimensions $11.168 \times 9.575 \text{ \AA}$. The 12 water molecules are located in the middle of the two $[\text{Zn}_4(\text{bpy})_4]$ squares of the box and are in a dish-like arrangement. The average $\text{O}\cdots\text{O}$ distance is 2.761 \AA , which is similar to that in the reported supramolecular $(\text{H}_2\text{O})_{12}$ morphology^{5c,e} and very close to the corresponding value 2.759 \AA in ice I_h .¹⁴ In our $(\text{H}_2\text{O})_{12}$ cluster, the average $\text{O}-\text{O}-\text{O}$ angle is 121.65° , which is similar to that found in the $(\text{H}_2\text{O})_{18}$ -based supramolecular water layer^{5d} but larger than that in the supramolecular $(\text{H}_2\text{O})_{12}$ morphology.^{5c,e} The separation of the $(\text{H}_2\text{O})_{12}$ clusters along the c axis is 9.575 \AA , which is equal to the length of the box. The 1D metal–organic nanotube possesses a square nanopore with the dimensions being $11.168 \times 11.168 \text{ \AA}$ (from Zn to Zn atom, Figure 1). All of the $-\text{NH}_2$ groups of the ATIBDC ligand point toward different directions, and the nanotubular framework looks like a screw propeller along the c axis (Figure 1).

It is especially interesting to note that **MONT-1** can remain crystalline at high temperature and the $(\text{H}_2\text{O})_{12}$ clusters can be reversibly trapped by the $\text{Zn}_8(\text{bpy})_8(\text{ATIBDC})_4$ box. TGA measurement reveals that the gradual weight loss of 7.0% from 50 to 150 °C corresponds to the loss of three uncoordinated water molecules (calcd: 6.5%). There is no weight loss from 150 to 340 °C, and after 340 °C, **MONT-1** starts to decompose. The crystals of **MONT-1** were heated at 180, 200, 240, and 280 °C in the air for 1 h to desolvate them and then cooled down to room temperature, and the crystal color changed gradually from light yellow to dark brown (Supporting Information). Single-crystal X-ray diffraction on these crystals reveals that the $(\text{H}_2\text{O})_{12}$ clusters are reabsorbed in the $\text{Zn}_8(\text{bpy})_8(\text{ATIBDC})_4$ box (Figure 2), although the shape of the cluster and the $\text{O}\cdots\text{O}$ distance are slightly changed (Supporting Information). The average $\text{O}\cdots\text{O}$ distance in the $(\text{H}_2\text{O})_{12}$ cluster changed from 2.761 \AA in the as-synthesized crystal to 2.710, 2.775, 2.790, and 3.209 \AA in the crystals after heating to 180, 200, 240, and 280 °C and cooling back down to room temperature in the air,

respectively. These results indicate that the adsorption is reversible and fast; the $(\text{H}_2\text{O})_{12}$ cluster has already been reabsorbed in the nanotube when the crystals were cooled back down to room temperature in the air.¹⁵

In summary, by using mixed organic ligands, a novel metal–organic nanotube has been synthesized and characterized. The new nanotubular material can keep crystalline even after heating to 280 °C for 1 h, which is quite rare in porous materials. The unique property of **MONT-1** is its reversible and fast adsorption of the $(\text{H}_2\text{O})_{12}$ cluster. To the best of our knowledge, **MONT-1** represents the first independent 1D metal–organic nanotube that can reversibly trap the $(\text{H}_2\text{O})_{12}$ cluster. Further studies will focus on the synthesis of other metal–organic nanotubes that can trap small water clusters.

Acknowledgment. This work was supported by National Nature Science Foundation of China (Grant 20701025).

Supporting Information Available: Experimental procedures, structural figures, and TGA as well as crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA805920T